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Nitrous oxide emissions increase exponentially when optimum nitrogen fertilizer rates are exceeded in the North China plain

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Abstract

The IPCC assume a linear relationship between nitrogen (N) application rate and nitrous oxide (N_2O) emissions in inventory reporting, however, a growing number of research studies show a nonlinear relationship under specific soil-climatic conditions. In the North China plain, a global hotspot of N_2O emissions, covering a land as large as Germany, the correlation between N rate and N_2O emissions remains unclear. We have therefore specifically investigated the N_2O response to N applications by conducting field experiments with five N rates, and high-frequency measurements of N_2O emissions across contrasting climatic years. Our results showed that cumulative and yield-scaled N_2O emissions both increased exponentially as N applications were raised above the optimum rate in maize (*Zea mays* L.). In wheat (*Triticum aestivum* L.) there was a corresponding quadratic increase in N_2O emissions with the magnitude of the response in 2012-13 distinctly larger than that in 2013-14 owing to the effects of extreme snowfall. Existing empirical models (including the IPCC approach) of the N_2O response to N rate have overestimated N_2O emissions in the North China plain, even at high rates of N use. Our study therefore provides a new and robust analysis of the effects of fertilizer rate and climatic conditions on N_2O emissions.

Keywords: N_2O emission, optimum N fertilizer rate, wheat-maize double cropping system, extreme weather event, freeze-thaw cycle, the North China plain

Introduction

Nitrous oxide (N_2O) is a long-lived potent greenhouse gas with a global warming potential 265 times greater than carbon dioxide (CO_2) over a 100-yr time scale and is the most significant ozone (O_3)-depleting substance in the atmosphere.[1-3] Anthropogenic emissions have led to a 20% increase in the level of N_2O in atmosphere since pre-industrial periods.[4] Agriculture is currently the largest anthropogenic source of N_2O accounting for two-thirds of the total anthropogenic emissions, which are mainly a consequence of the use of synthetic N fertilizer and animal manure.[4]

The application of synthetic nitrogen (N) fertilizer is necessary to achieve the high levels of crop production that are required to feed a large and increasingly affluent global population.[4-5] China consumes about 30% of global N fertilizer,[6] and was responsible for 28% of the world's synthetic fertilizer induced N_2O emissions in 2015.[7] Between 2000-2007, synthetic N fertilizer use produced 77% of the total direct N_2O emissions from Chinese agricultural soils.[8] Overuse of N fertilizers is the main factor causing high levels of N_2O production and other reactive N losses to environment in China.[9-10]

The amount of N fertilizer applied to crops is the most significant single predictor of N_2O emissions and changing fertilizer application rates therefore provides an effective means for decreasing emissions without disrupting crop rotations or local farming practices.[11-13] However, relationships between N rates and N_2O emissions have not been characterized in a consistent way by previous studies. In estimating N_2O emissions induced by N fertilization, the IPCC uses empirical relationships between N_2O emissions and N inputs with a default Tier 1 emission factor of 1% (and an uncertainty of 0.3-3%). This approach ignores spatial and temporal variabilities resulting from soil type, climate, crop and management, i.e. 1% of the applied N emitted as N_2O from all drained agricultural soils.[14] This emission factor was developed from a large and variable global dataset, and thus couldn't reflect the heterogeneity of local conditions. In addition, a single emission factor implies a linear relationship between N_2O emissions and N rates ignoring the sink capacity of the crop and soil. Lately, this approach has been challenged by the availability of high frequency and more precise field observations.[15-19] A meta-analysis of global data compiled of 78 publications covering 233 site-years that had used more than two N rates and a zero N treatment found there was an exponential increase in N_2O emissions as the N rate exceeded crop demand.[20] A study of corn with six rates of N fertilizer (0-225 kg N ha^{-1} $season^{-1}$) at five farm sites in Michigan, USA over two years, also found overall exponential responses of N_2O emissions to N rates at a given site across different years.[21] Numerous field measurements in the North China plain have shown N_2O emission factors were generally in the range 0.08-0.21% for wheat (*Triticum aestivum* L.), 0.44-0.59% for maize (*Zea mays* L.) and 0.10-0.59% for wheat-maize cycle, which were all well below the default IPCC emission factor (1%).[9,22-26]

Relationships between N_2O emissions and N rates established by direct N_2O measurements under specific soil-climate conditions, cropping systems and agronomic management are crucial for making more accurate national inventory assessments and developing more targeted mitigation measures. It is particularly important in China given its wide spatial variation of N fertilizer use, crop types and soil-climatic conditions across the arable sector which contribute to the development of hotspots of N_2O emissions such as the North China plain.[27-28]

As a major cereal producing area in China, the North China plain covers 300,000 km^2 which is almost equivalent to the land area of Germany (350,000 km^2), and more than 70% of its cropland is over-fertilized with synthetic N fertilizer inputs of up to 550-600 kg N ha^{-1} yr^{-1} for the intensive wheat-maize double cropping systems,[9,29] which leads to N_2O emissions in this region that are higher than those in other regions in China.[8-9,27-28,30-31]

Nevertheless, the relationships between N rates and N_2O emissions in the North China plain remain unclear. A meta-analysis of direct N_2O measurements in this region has shown an exponential relationship between emissions and N applications to maize and wheat,[32] while two field experiments recently reported linear relationships for these crops.[26,33] However, neither of these studies focused specially on relationships between N rates and N_2O emissions, but instead looked wider effects of other soil and management variables on emissions. Hence, there is a requirement for studies that focus on the response of N_2O

emissions to N rates to establish reliable models for estimating the total N_2O emissions in the North China plain.

The objectives of present study were: (1) to obtain high-frequency field measurements of N_2O fluxes in response to N rates across diverse climatic years by controlling other soil and management variables; (2) to determine the response of cumulative or yield-scaled N_2O emissions to N rate in wheat, maize and annual wheat-maize cycle; (3) to compare the N_2O response model in this study with models at other sites in the North China plain and at the global scale.

Materials and Methods

Experiment site and design

The study site was located at the Quzhou research station (36.87°N, 115.02°E) of the China Agricultural University in Hebei province, which represents typical soil-climatic conditions and crop management practices of the North China plain,[34-36] as shown in S1.1 of Supporting Information (SI). This study was based on a long-term field experiment established in October 2007, which was designed to assess the optimum N rate for relatively high target crop yields whilst concomitantly minimizing environmental risks by monitoring crop N demand and soil N supply (nitrate-NO_3^- content in root zone) at key growth stages. It included five N fertilizer rates: (1) CK, no fertilizer as a control; (2) Opt.*0.7, 70% of optimum N fertilizer rate; (3) Opt., optimum N fertilizer rate determined by the real-time NO_3^- monitoring method; (4) Opt.*1.3, 130% of optimum N fertilizer rate; (5) Con., local conventional N rate.

The optimum N rate was determined by in-season root zone N management[37-39] which subtracted soil NO_3^--N content in the root zone from target N values at key growth periods. Winter wheat was divided into two periods, i.e. from sowing to stem elongation and from stem elongation to harvest. Root zone depths for these two periods were identified as 0-60 cm and 0-90 cm, respectively. Summer maize was separated into three periods, i.e. from sowing to the six-leaf stage, from the six-leaf stage to the ten-leaf stage and from the ten-leaf stage to harvest. Root zone depths in these three periods were 0-30, 0-60 and 0-90 cm. The target N value was calculated as the sum of N uptake by shoots and roots in each growing period for a target grain yield and N content. Conventional farming N rates were 250 kg N ha^{-1} for maize (100 kg N ha^{-1} applied at three-leaf stage and 150 kg N ha^{-1} applied at ten-leaf stage) and 300 kg N ha^{-1} for wheat (150 kg N ha^{-1} before sowing and 150 kg N ha^{-1} at the stem elongation stage).[40-41]

We carried out our study with these five N rates ranging from 0 to 550 kg N ha^{-1} yr^{-1} over two wheat-maize cycles from June 2012 to June 2014, and measured N_2O emissions, soil temperature, moisture, mineral N content, crop yield and above-ground N uptake. Each treatment was replicated four times in a randomized block arrangement with an area of 300 m^2 (20 m*15 m) per plot. Urea was used as the N source as it is the main N fertilizer used by farmers in the North China plain.[6] See field and crop managements in S1.2 of SI.

Measurement of N_2O emission

Gas sampling took place over the two rotation cycles from June 2012 to June 2014, using the closed static chamber method (See S1.3 in SI).[42-43] Gas samples were collected between 8:30 and 11:30 in the morning of each sampling day. Four 20 ml headspace samples were taken using a 50 ml plastic gas tight syringe at 0, 15, 30, and 45 min after chamber closure. The syringes were flushed with chamber air three times prior to the samples being taken. N_2O concentrations were analyzed by a gas chromatograph (Shimadzu GC-14B, Kyoto, Japan) equipped with an electronic capture detector (ECD) within 24 h after sampling. We injected 10 ml gas samples into the GC. High-purity dinitrogen (N_2) (99.999%) was used as the carrier gas for N_2O analysis and 10% CO_2 in pure N_2 was used as a buffering gas for the ECD. Two filter columns of 2 mm inner diameter, filled with Porapak (80/100 mesh), were used to separate N_2O from oxygen (O_2) and water vapour for the ECD. The detection limit of N_2O emission was 2 μg N m^{-2} h^{-1}.[26,44-45] We used known concentrations of mixed gas (0.333 ppm N_2O in pure N_2) to calibrate the gas samples during each measurement cycle.[26,33,44]

Gas sampling was undertaken daily for 10 days after fertilization and 3 days after irrigation or rainfall (＞20 mm). For the remaining periods, gas was sampled every 4 days, except in winter when the gas was sampled weekly.

Measurements of auxiliary parameters

Soil samples for measurements of water-filled pore space (WFPS) and mineral N (ammonium-NH_4^+, NO_3^-) were taken at 1, 3, 5, 7, 9 and 11 days after fertilization, 1 and 3 days after irrigation or rainfall (＞ 20 mm). For the remaining periods, soil was sampled every 2 gas samplings, and each soil sampling was accompanied by a N_2O measurement. Soil WFPS was measured by the oven-drying method. Soil mineral N was extracted by 0.01 mol L^{-1} calcium chloride ($CaCl_2$) solution and analyzed by an automated NH_4^+ and NO_3^- analyzer (See S1.4 in SI). Climate data including air temperature and precipitation were provided by the weather station at this study site. Grain yield and above-ground N uptake in 2012-13 and 2013-14 wheat were reported by Lu et al.[46] Corresponding data in 2012 and 2013 maize were recorded from Yan (See S1.5 in SI).[40] The N surplus in our study was defined as the sum of N fertilization, N deposition and biological N fixation minus above-ground N uptake. N deposition in Quzhou was 63 kg N ha^{-1}.[47] Biological N fixation was assumed to be 5 kg N ha^{-1} $season^{-1}$.[48]

Calculations of N_2O emission

N_2O flux was calculated as follows:

$$F = k_1 \times \frac{P_0}{P} \times \frac{273}{273 + T} \times \frac{M}{V} \times H \times \frac{dc}{dt} \qquad (1)$$

where F (μg N_2O-N m^{-2} h^{-1}) is the flux, k_1 (0.001) is a coefficient for unit conversion, P_0 (hPa) is atmospheric pressure in the chamber, P (1013 hPa) is standard atmospheric pressure at this site, T (°C) is mean air temperature in the chamber, M (28 g N_2O-N mol^{-1} N_2O) is the molecular weight of N_2 , V (22.4 L mol^{-1}) is the mole volume at 273 K and 1013 hPa, H (m) is the chamber height, c (μL L^{-1}) is the concentration of N_2O as volume mixing ratio, t (h) is the time of chamber closure, dc/dt ($\mu L\ L^{-1}\ h^{-1}$) is the rate of change in N_2O concentration after chamber closure. Here dc/dt was given by a linear or exponential regression model. The result was accepted when it was significant at $P < 0.05$.[49] If linear and exponential regression models were both significant, we chose the exponential model when R^2 was higher than that of the linear model.[26,49]

A linear interpolation method was used to estimate N_2O emission on non-sampling days between every two gas samplings and further determine cumulative N_2O emission for a growth season or a rotation cycle through the summation of daily emissions.[50-51] The period from sowing to next crop sowing was used as the duration for calculating seasonal cumulative emissions and emission factors of each crop, for two maize seasons from 18th June to 6th October and for two wheat seasons from 8th October to next 15th June.

Yield-scaled N_2O emissions have been proposed as an indicator that is able to capture both crop productivity and environmental costs when assessing optimal N rate.[52] In our study, yield-scaled N_2O emissions were determined as follows:

$$N_2O_{\text{yield-scaled}}\ (\text{g } N_2O\text{-N kg}^{-1}\text{ grain}) = \frac{\text{cumulative } N_2O \text{ emission (kg N ha}^{-1})}{\text{grain yield (t ha}^{-1})} \qquad (2)$$

The direct N_2O emission factor for fertilizer N was calculated by following equation:

$$EF_{N2O} = \frac{N_2O_{fer} - N_2O_{ck}}{N_{fer}} \times 100 \qquad (3)$$

where EF_{N2O} (%) is direct N_2O emission factor, N_2O_{fer} and N_2O_{ck} are cumulative N_2O emissions (kg N_2O-N ha^{-1}) from N fertilized treatments and the no fertilizer treatment accordingly, N_{fer} is the rate of N applied to soil (kg N ha^{-1}).

Statistical analysis

We performed linear, quadratic and exponential curve fittings to simulate the response of N_2O emission to N rates, then used the coefficient of determination (R^2) and variance (SST-sum of squares for total, SSR-sum of squares for regression, SSE-sum of squares for error) to evaluate their confidence. We firstly selected the function with the highest R^2 value at $P <$

0.05 for least significant differences (LSD), and when R^2 values were same among these fittings, a lower SSE value (meaning a lower systematic error) was used as the best N_2O responding function. Differences in cumulative N_2O emission, yield-scaled N_2O emission and grain yield among all treatments were analyzed by a One-way Anova procedure for LSD at $P < 0.05$. Statistical analyses were undertaken using IBM SPSS Statistics 21 (SPSS Inc., Chicago, IL, USA) and SigmaPlot 12.5 (Systat Software Inc., Erkrath, Germany).

Results

Overall climate conditions in the two years measurement years

There was a particularly cold winter in 2012-13. Compared to the long-term average annual air temperature (13.2 °C) and precipitation (473 mm), 2012-13 was both colder and wetter with an average temperature of 12.7 °C and precipitation of 581 mm. By contrast, the 2013-14 cycle had a slightly higher temperature of 14.6 °C and more normal precipitation of 470 mm (Figures 1 (a) and S7 (a)). Warm and wet conditions were concentrated in the maize season (June-September) with a mean air temperature of 23.3 °C and precipitation of 430 mm in the 2012 maize, and correspondingly 25.7 °C and 369 mm in the 2013 maize. However, a large variation occurred between the two wheat seasons. In the 2012-13 wheat, there was an extreme snowfall event with 65.8 mm precipitation and minimum air temperature of -10 °C, leading to a lower mean air temperature (7.1 °C) and above average precipitation (151 mm) in comparison with 7.4 °C and 101 mm in the normal 2013-14 wheat. There were also significant freeze-thaw cycles in the winter period (December-February) of the 2012-13 wheat.

N_2O emission responding to soil temperature, moisture and mineral N

Large emission peaks (>500 μg N_2O-N m^{-2} h^{-1}) consistently occurred in the N treatments within one week after fertilization following rainfall or irrigation in the maize seasons. There was also a short flush of N_2O resulting from the drying-wetting cycle induced by an irrigation of 90 mm after sowing maize in June 2012 (Figure 1 (b)). The conventional treatment was associated with the highest N_2O emissions ranging from 1200 to 3400 μg N_2O-N m^{-2} h^{-1}, and the largest N_2O flux (3400 μg N_2O-N m^{-2} h^{-1}) was observed in the coupled fertilization, irrigation and deep plough after planting maize in June 2013. These large N_2O emissions occurred under hot and wet conditions when the soil WFPS ranged from 60% to 80%, and the soil temperature at 5 cm depth was between 20-30 °C (Figures 1 (a) and S1 (a)), Within these ranges of soil moisture and temperature, the magnitude of daily N_2O fluxes corresponded well with rates of N application with highest emissions of 100, 200 and 250 g N_2O-N ha^{-1} day^{-1} in Opt., Opt.*1.3, and Con. treatment, respectively (Figure S2). Two N_2O peaks lower than 500 μg N m^{-2} h^{-1} occurred after fertilization in the maize seasons when emissions were restricted by dry soil conditions (40% WFPS) in July 2012 and by low topdressing N rates (20-39 kg N ha^{-1} for Opt.*0.7, Opt. and Opt.*1.3 treatments) in August 2013 (Table 1).

In the wheat seasons, due to the limitation of soil moisture (15-40% WFPS) and temperature (average around 7 °C), N_2O peaks were all below 200 μg N_2O-N m^{-2} h^{-1} even with high soil NH_4^+ or NO_3^- concentrations following each fertilization. However, there was a peak in N_2O emissions ranging from 200 to 500 μg N_2O-N m^{-2} h^{-1} and lasting over one month under the freeze-thaw cycles following the extreme snowfall in the 2012-13 wheat.

Soil NH_4^+ and NO_3^- contents of the conventional treatment were the highest reaching 20-60 and 50-200 mg N kg^{-1}, respectively, after fertilizations in the two maize seasons and once in 2013-14 in the wheat season (Figure S1 (b)-(c)). An irrigation event in December 2012 gave rise to a small pulse of NH_4^+ and NO_3^- by alternate drying and wetting. During the two wheat-maize cycles, N_2O emissions and soil mineral N contents in the control treatment remained at very low levels, below 70 μg N_2O-N m^{-2} h^{-1} and 20 mg N kg^{-1}, respectively.

Changes in soil mineral N content were not always synchronized with N_2O fluxes although they were proportional to increases in N rates following a quadratic response curve. The cumulative N_2O emissions also showed a quadratic response with rising mineral N contents in both wheat, maize and the annual wheat-maize cycle (Figure S3).

Cumulative and yield-scaled N_2O emissions under increasing N rates

Cumulative and yield-scaled N_2O emissions both increased stepwise as N rates increased, and showed remarkable interannual variation due to high N_2O emissions following the extreme snowfall in 2012-13 wheat (Figure S4 (c)-(f)) (See grain yields in S2.1 of SI). Cumulative N_2O emissions from N fertilized treatments ranged from 1.3 to 3.7 kg N_2O-N ha^{-1} in maize in both years, but they were between 2.2 and 4.3 kg N_2O-N ha^{-1} in 2012-13 wheat and 7 times higher than that in 2013-14 wheat ranging from 0.3 to 0.6 kg N_2O-N ha^{-1} in the N fertilized treatments. The optimum N rate had significantly lower N_2O emissions when compared with the conventional rate by 41-59% and 33-38% in maize and wheat ($P<0.05$), respectively, but achieved similar crop yields. Meanwhile, it didn't significantly increase N_2O emissions compared with the 70% of Optimum treatment ($P<0.05$) except in the 2012-13 wheat.

Yield-scaled N_2O emissions from N fertilized treatments ranged from 0.15-0.38 g N_2O-N kg^{-1} grain of maize in both two years (Figure S4 (e)-(f)), but they amounted to 0.30-0.50 g N_2O-N kg^{-1} grain in the extreme 2012-13 wheat and were over 6 times higher than that in the normal 2013-14 wheat (0.05-0.08 g N_2O-N kg^{-1} grain). Consequently, annual yield-scaled N_2O emissions in 2012-13 (0.22-0.42 g N_2O-N kg^{-1} grain) were nearly 2 times higher than those in 2013-14 (0.10-0.24 g N_2O-N kg^{-1} grain). The Optimum treatment significantly decreased yield-scaled N_2O emissions from the Conventional treatment by 42-61% and 31-38% in maize and wheat ($P<0.05$), respectively. Notably, yield-scaled N_2O emissions from the no N fertilizer treatment were larger than all fertilized treatments in 2013-14 wheat, which was caused by low grain yield.

On an annual basis, compared to the conventional N rate (550 kg N ha^{-1} yr^{-1}), the optimum N rate (360 kg N ha^{-1} yr^{-1}) decreased cumulative and yield-scaled N_2O emissions by 35% (4.9 vs. 7.6 kg N_2O-N ha^{-1}) and 37% (0.26 vs. 0.41 g N_2O-N kg^{-1} grain), while maintaining crop yields (18.5 vs. 18.4 t ha^{-1}) in the extreme weather of 2012-13. During the more normal year of 2013-14, cumulative and yield-scaled N_2O emissions were lowered by 57% (1.8 vs. 4.2 kg N_2O-N ha^{-1}) and 54% (0.11 vs. 0.24 g N_2O-N kg^{-1} grain) but yields were relatively constant (17.5 vs. 17.4 t ha^{-1}). In the treatment receiving 70% of the optimum N rate (240-252 kg N ha-

^{1} yr^{-1} of Opt.*0.7), there was a significant drop in crop yield (17.1 t ha^{-1} in 2012-13 and 15.7 t ha^{-1} in 2013-14), however, it didn't significantly decrease yield-scaled N_2O emission (0.21 and 0.10 g N_2O-N kg^{-1} grain in 2012-13 and 2013-14, respectively). As for the elevated optimum N rate (445-469 kg N ha^{-1} yr^{-1} of Opt.*1.3), it resulted in a rise of yield-scaled N_2O emission (0.31 and 0.17 g N_2O-N kg^{-1} grain in 2012-13 and 2013-14, respectively), without significantly increasing crop yield (18.2 t ha^{-1} in 2012-13 and 17.6 t ha^{-1} in 2013-14). Therefore, the optimum N rate could achieve the high targeted yield but with lower cumulative and yield-scaled N_2O emissions.

In conclusion, our results have demonstrated that applying the optimum N rate to wheat-maize systems in the North China plain could allow conventional N applications to be reduced by 37% (350 vs. 550 kg N ha^{-1} yr^{-1}), leading to a reduction in cumulative N_2O emissions of 42% (3.5 vs. 6.0 kg N_2O-N ha^{-1}) and reduction in yield-scaled N_2O emissions of 44% (0.18 vs. 0.32 g N_2O-N kg^{-1} grain) while maintaining crop yield (18 t ha^{-1}) and achieving a slightly positive N surplus (18-37 kg N ha^{-1} yr^{-1}). Regarding the other two adjusted optimum N levels, the decrease of N input (246 kg N ha^{-1} yr^{-1} for Opt.*0.7) was accompanied by a significant drop in crop yield rather than N_2O emissions, and the increase of applied N (457 kg N ha^{-1} yr^{-1} for Opt.*1.3) resulted in a rise in N_2O emissions rather than crop yield.

The relationship between N_2O emissions and N rates

We explored linear, quadratic and exponential models of the relationship between N_2O emissions and N rates and analyzed their R^2 and variance to determine the best model of cumulative and yield-scaled N_2O emission to N rate. Since N_2O emission patterns for the two wheat seasons varied, we developed N_2O emission models for each wheat season and each annual rotation cycle. Because N_2O emission patterns for the two maize seasons were broadly similar, we combined the data to develop the general N_2O emission models for maize (Figure 2). The exponential model had the highest R^2 and lowest SSE for maize but in each wheat season, the quadratic model provided a better fit (Table S1 and S2).

For the maize season and on an annual basis, cumulative and yield-scaled N_2O emissions both increased exponentially as N rate increased, especially at N rates exceeding the optimum (Figure 2). The N_2O emissions from the conventional N rate were more than double the emission from optimum rate. In the wheat seasons, N_2O emissions increased quadratically with rising N rates, but the magnitude and strength of the response in the extreme 2012-13 wheat season was distinctly larger than that in the normal 2013-14 season owing to the effects of freeze-thaw cycles. Thus, the slow increases in emissions in response to increasing N rates in 2013-14 was more typical for wheat seasons in the North China plain (see more in discussion section). N_2O emission factors under increasing N rates are shown in S2.2 of SI.

We explored further the responses of crop yield, above-ground N uptake and N_2O emissions together to N rate (Figure S5; See discussion in S3.1 of SI) and the correlations between N_2O emission and N surplus (Figure S6). There was a quadratic relationship between crop yield or above-ground N uptake and increasing N rates both in the extreme snowfall year and the normal year. The yield and N uptake reached close to the maximum at the optimum N rate and showed a decrease gradually above that, but N_2O emissions increased exponentially when the optimum rate was exceeded.

N_2O emissions increased nonlinearly (in both quadratic and exponential patterns) as the N surplus rose from -50 to 220 kg N ha^{-1} yr^{-1} (Figure S6). Where the N surplus was lower than zero, both cumulative and yield-scaled N_2O emissions remained stable and relatively low. The optimum N rate had a slightly positive N surplus of 37 and 18 kg N ha^{-1} yr^{-1} in the extreme snowfall and normal year, respectively, but did not significantly increase the cumulative and yield-scaled N_2O emissions. However, the N surplus at the conventional N rate ranged from 210 to 220 kg N ha^{-1} yr^{-1} and resulted in exceptionally high cumulative and yield-scaled N_2O emissions.

Discussion

Comparison of modelling approaches

This study provides clear evidence of an exponential rise in N_2O emissions at N fertilizer rates higher than the optimum level, which means that N_2O emissions per unit input of N fertilizer also became larger. Previous studies with gradients of N addition to maize in Michigan USA indicated that N_2O fluxes mainly responded to N additions that exceeded the crop demand, and also found an exponential response of N_2O emissions to N rates, in which N_2O fluxes were significantly increased by 43-115% after fertilization above the recommended N rate (135 kg N ha^{-1}).[15,21] More discussion of mechanisms underlying the exponential response of N_2O emissions to N rates is provided in S3.2 of SI.

The Global N_2O response model for upland grain crops and IPCC's emission factor model both overestimated the N_2O emissions, even at excessive N rates in both maize and wheat (Figure 3 and Table S4). This contradicts previous studies that have reported underestimation of N_2O emissions at high N application rates.[20-21] With conventional N application rates (250-300 kg N ha^{-1} $season^{-1}$), the two global models calculated N_2O emissions to be close to our model in maize but overestimated N_2O emissions by 6-8 times (0.6 vs. 4.0-4.8 kg N_2O-N ha^{-1}) in wheat in the normal year. In the optimum N range (150-180 kg N ha^{-1} $season^{-1}$) (Figure 3),[9,44,53] N_2O emissions were overestimated by 60% (1.7 vs. 2.6-2.8 kg N_2O-N ha^{-1}) in maize and by 7 times (0.4 vs. 2.6-2.8 kg N_2O-N ha^{-1}) in wheat of the normal year. Nevertheless, the two global models both gave realistic estimations of the peak of N_2O emissions from wheat in the extreme snowfall year.

This overestimation occurred mainly because the global models used a statistical description of previous high emission data mostly measured in Europe or North America,[12,20,54-56] but were not representative of the relatively low N_2O emissions observed in the North China plain. Many recent studies have shown that N_2O is mainly produced through nitrification with little denitrification due to the low carbon calcareous soils and lack of moisture that is prevalent in the North China plain and the Mediterranean regions.[22,57-60] In our study, the N_2O emission peaked and soil NO_3^- concentration increased after NH_4^+-based fertilizer (urea) application. During this period nitrification would have predominated driven by the high pH soil, and moisture contents around 60%-80% of soil WFPS in the whole maize season and April in wheat season, which was consistent with previously results that demonstrated that nitrification and nitrifier denitrification were the major source processes. However, N_2O emissions after fertilization in wheat was sow at the beginning of October were lower than in the maize season mainly because of limited soil moisture (around 40-50% of WFPS[22,57]). This contrasts with some regions that are dominated by denitrification (e.g. UK and Germany) with a higher ratio of N_2O to N_2O+N_2.[22,61-62] Overestimation of N_2O emissions by IPCC modelling was also reported in a well-managed, high input, high yielding irrigated maize system in Nebraska, USA, in which the global warming potential was estimated to be 28% higher than that based on the exponential model proposed by Van Groenigen et al.[52,63]

The statistical model using a meta-analysis of data from the North China plain,[64] predicted slightly higher N_2O emissions than our model (difference within 0.5 kg N_2O-N ha^{-1}) at an N rate of up to 220 kg N ha^{-1} in maize, but above this, our predictions were higher than that of the statistical model. The difference between two models could be attributed to the large and varied dataset, which included not only the N rate, but also soil and climatic variables from the different sites. N_2O emissions calculated by the models on a site-specific basis, but over multiple-years of field measurements in the North China plain were similar to the values calculated by our model below the optimum N rate.[26,33] But they significantly underestimated N_2O emissions when N rates exceeded the optimum level in maize, and at the conventional N rate, they underestimated emissions by more than 50% (1.5-1.8 vs. 3.6 kg N_2O-N ha^{-1}). This underestimation was probably a consequence of changes in other management factors (e.g. straw return; alternative cropping and the rotation system) significantly decreasing N_2O emissions at high N rates. Nevertheless, the estimations of N_2O emissions in wheat were consistent among all these models with the relatively low values in a normal year, but large discrepancies in the extreme winter year.

N_2O emissions induced by freeze-thaw cycles

During the winter period (December-February) in the extreme snowfall year (Figure S7; See S3.3 in SI), cumulative N_2O emissions from N fertilized treatments were 1.7-3.3 kg N_2O-N

ha^{-1} which accounted for 30-48% of the annual N_2O emission. However, in the normal year, they were only 0.10-0.15 kg N_2O-N ha^{-1} and accounted for 3-6% of the annual N_2O emission, which was more typical of the North China plain (Figures 1 (b) and S4 (c)-(d)). Freeze-thaw cycles were important factors in driving the peaks in N_2O emissions, which were mostly attributed to the newly produced N_2O by microbial processes in the surface layer rather than the release of N_2O trapped in the deep unfrozen layer (See S3.4 in SI).[65] Although the extreme winter significantly increased N_2O emissions, it didn't reduce crop yields or above-ground N uptake in this wheat-maize cycle (Figures S4 (a)-(b), S5 (b)-(e)).

Extreme weather events including intense snowfall in winter and heavy rainfall in summer have increased across China over the last 50 years, with large geographical variations.[66-68] The impacts of extreme weather events on regional N_2O emissions need to be considered in the context of global climate change, since intense snowfall can give rise to so large increases in N_2O over short time periods as a consequence of freeze thaw cycles, and heavy rainfall can contribute to significant peaks of N_2O emission due to high NO_3^- accumulation in the soil profile which is widespread in the North China plain.[22,69-70] Because we measured N_2O emissions over two years covering an extreme winter and a normal year, our results were representative in this cropping system in the North China plain given the high frequency of gas and soil samplings, and comparisons with other studies in multiple years and sites in this region. This helps to provide a robust understanding and prediction of the impact of climate change on one of the world's hotspots of N_2O emissions.

Implications for both model update and sustainable N management

Nitrogen inputs in intensively managed cropping systems should aim to achieve high target crop yields whilst simultaneously sustaining soil N pools and reducing environmental impacts.[71] Previous studies have shown that significant decreases in N_2O emissions could be achieved by reducing excessive N inputs and soil N surpluses without sacrificing crop yields.[21,72-73] Hence, instead of seeking the maximum crop yield by excessive N inputs which lead to unnecessary N_2O emissions, balancing the crop demand for N with the supply could achieve maximal economic return and positive environmental outcomes.[50,52,74] Our results showed that N_2O emissions increased nonlinearly (in both quadratic and exponential patterns) as the N surplus rose, which was in line with the result from a meta-analysis of 48 maize and 40 wheat field experiments across China.[73] The key to mitigating N_2O emissions from fertilizer-N is to reduce the N surplus rather than decrease N applications that may be counterproductive.[75] Meanwhile, N_2O emissions and other reactive N losses could be minimized by matching N supply and crop N uptake.[39,63] We here demonstrate that optimized N applications with a slightly positive N surplus are advisable for achieving higher target yields and sound environmental outcomes that fail to be achieved by the conventional farming approach used in this region.

Our results found the overestimation of N_2O emissions by previous studies in this region using global statistical models. The exponential model of global upland grain crops and the IPCC fixed emission factor model both gave much higher emission estimates when compared to our model in a normal weather year. To improve the estimation of N_2O emission and its mitigation potential it is crucial to use regional models that represent specific soil-climate conditions and cropping systems, then aggregate these different systems to make more accurate national inventory assessments. Total N_2O emissions from the North China plain should be reevaluated in the light of this research.

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Figure Captions

Figure 1. Dynamics of (a) air temperature, soil temperature at 5 cm depth, precipitation and irrigation; and (b) N_2O emission during the two wheat-maize cycles from June 2012 to June 2014. Solid and dashed arrows in (b) represent fertilization and tillage, respectively. Vertical bars in (b) indicate standard deviation (n=4).

Figure 2. Correlations between N application rates and cumulative N_2O emissions (a-c), and between N application rates and yield-scaled N_2O emissions (d-f). Data point refers to the value of each replicate during the two wheat-maize cycles from June 2012 to June 2014.

Figure 3. Comparison of N_2O responses to N application rates in our study site and other sites in the North China Plain or the global scale. Green shaded areas represent the optimum N application rate range (150-180 kg N ha^{-1} $season^{-1}$) for maize and wheat in the North China Plain.

Supporting Information

This file includes detailed site and soil-climate characteristics, field and crop managements, measurement methods, results and discussion of the second important points and supplementary tables and figures (Table S1 to S5, Figure S1 to S7).

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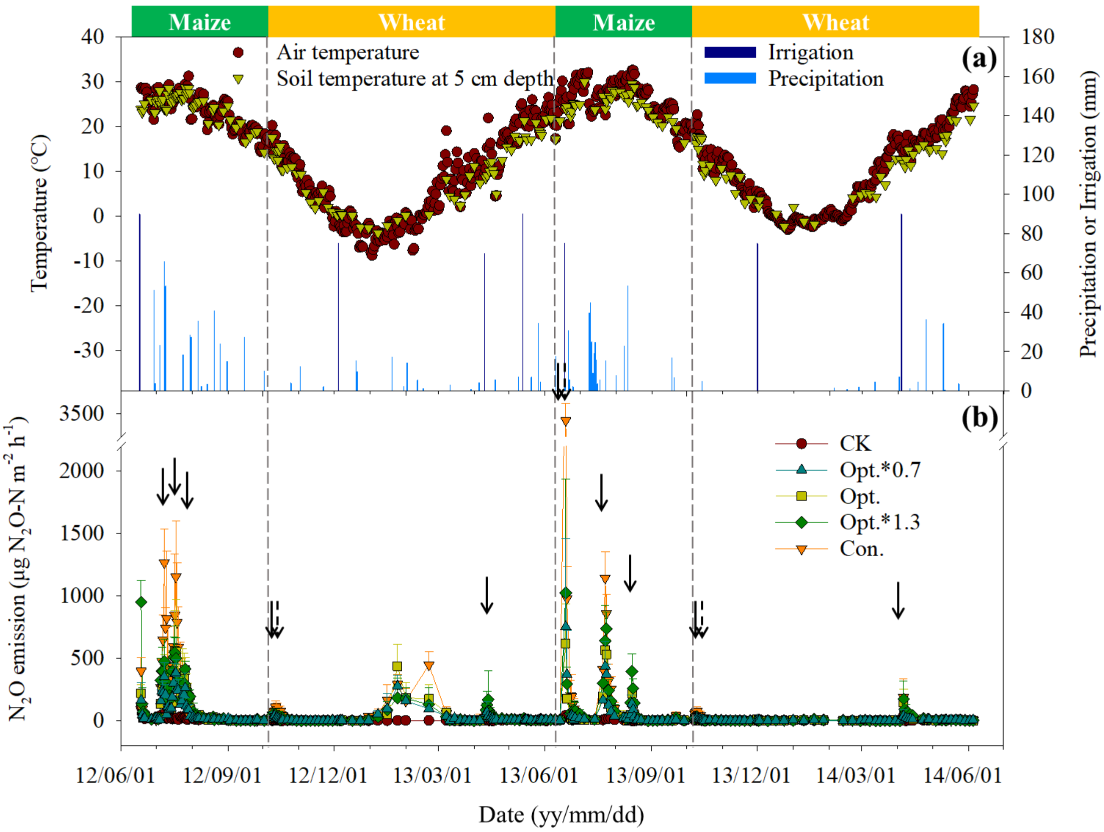

Figure 1. Dynamics of (a) air temperature, soil temperature at 5 cm depth, precipitation and irrigation; and (b) N_2O emission during the two wheat-maize cycles from June 2012 to June 2014. Solid and dashed arrows in (b) represent fertilization and tillage, respectively. Vertical bars in (b) indicate standard deviation (n=4).

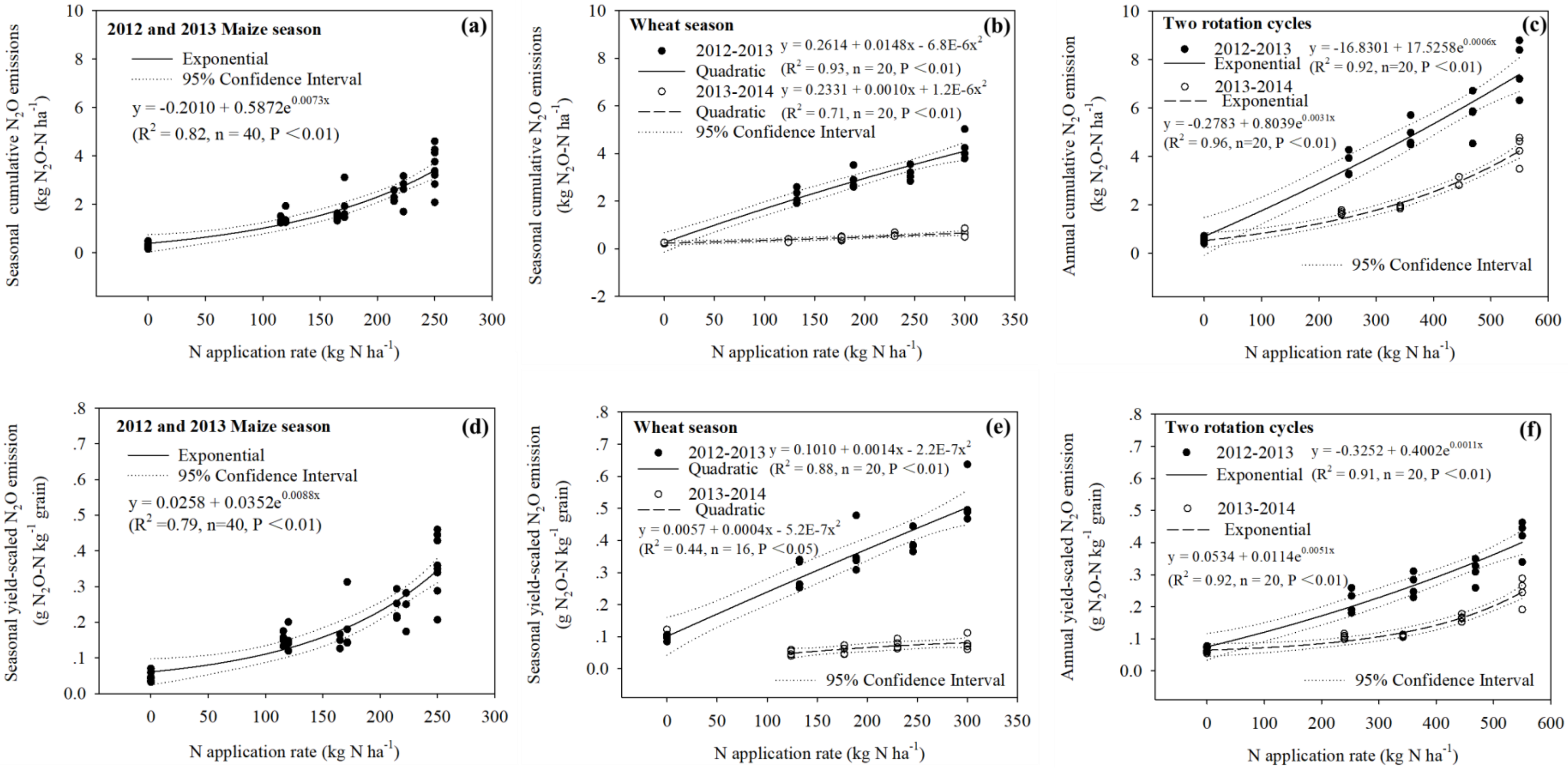

Figure 2. Correlations between N application rates and cumulative N_2O emissions (a-c), and between N application rates and yield-scaled N_2O emissions (d-f). Data point refers to value of each replicate during the two wheat-maize cycles from June 2012 to June 2014. The equations for each response in this figure are also shown in Table S5.

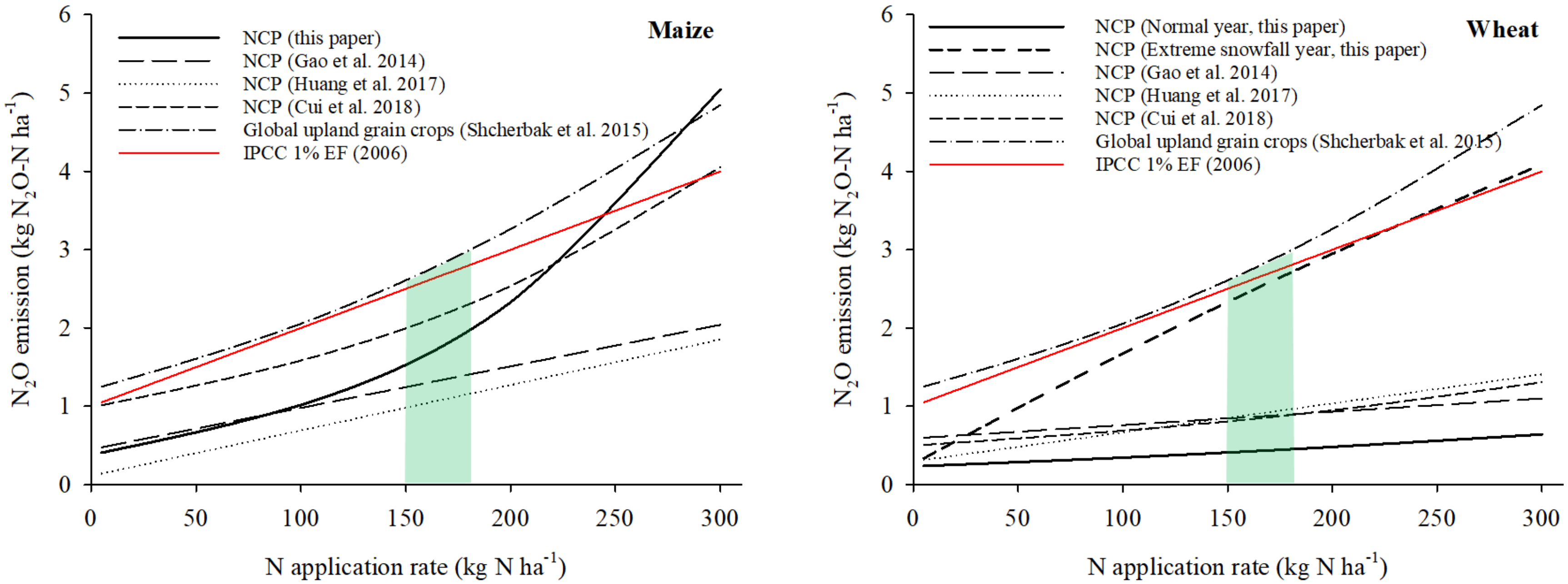

Figure 3. Comparison of N_2O responses to N application rates in our study site and other sites in the North China plain or the global scale. Green shaded areas represent optimum N application rate range (150-180 kg N ha^{-1} $season^{-1}$) for maize and wheat in the North China plain.

Table 1 N fertilization and irrigation rates in the two wheat-maize cycles.

Growth season	Date	N fertilization rate (kg N ha^{-1})					Irrigation rate (mm)
		CK[a]	Opt.*0.7	Opt.	Opt.*1.3	Con.	
2012 Maize (Sowing date: 16 Jun.)	17 Jun.						90
	3 Jul.	0	32	45	59	100	
	13 Jul.	0	48	69	89	150	
	21 Jul.	0	40	58	75	0	
	Total	0	120	172	223	250	90
2012-13 Wheat (Sowing date: 8 Oct.)	8 Oct. 2012	0	35	50	65	150	
	5 Dec. 2012						75
	10 Apr. 2013	0	97	139	181	150	70
	13 May. 2013						90
	Total	0	132	189	246	300	235
2013 Maize (Sowing date: 16 Jun.)	16 Jun.	0	32	45	59	100	
	18 Jun.						75
	19 Jul.	0	63	90	117	150	
	13 Aug.	0	21	30	39	0	
	Total	0	116	165	215	250	75
2013-14 Wheat (Sowing date: 7 Oct.)	7 Oct. 2013	0	35	50	65	150	
	1 Dec. 2013						75
	4 Apr. 2014	0	89	127	165	150	90
	Total	0	124	177	230	300	165

[a] Abbreviations are: CK-- no N fertilizer treatment, Opt.*0.7-- 70% of optimum N fertilizer rate, Opt.-- optimum N fertilizer rate, Opt.*1.3-- 130% of optimum N fertilizer rate, Con.-- conventional N fertilizer rate.

Abstract Art